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Re: 2

Process metallurgy

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Calculation of the interfacial properties of liquid steel – slag systems

Alan W. Cramb and Itaru Jimbo

The rates of many high temperature metallurgical reactions are strongly influenced by interfacial phenomena and to determine reaction rates it is necessary to have an accurate model of interfacial properties. In this article, the factors governing interfacial tension in slag-metal systems will be briefly discussed and, a model based on the combination of the Gibbs and Langmuir adsorption isotherms with Girifalco and Good's expression for the interfacial tension between immiscible liquids, will be shown to be consistent with current literature values and allow the calculation of both the interfacial tension and the contact angle between liquid slags and liquid iron in the $\text{CaO-CaF}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ system. The application of this approach to systems containing FeO in the slag and carbon in the metal are then discussed.

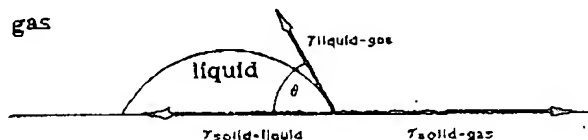
Berechnung der Grenzflächeneigenschaften in flüssigen Stahl-Schlacke-Systemen. Die Geschwindigkeiten vieler metallurgischer Reaktionen, die bei hohen Temperaturen ablaufen, werden stark durch Grenzflächenphänomene beeinflusst. Zur Bestimmung der Reaktionsgeschwindigkeiten ist daher ein genaues Modell der Grenzflächeneigenschaften notwendig. In der vorliegenden Arbeit werden die Faktoren, die die Grenzflächenspannung in Schlacke-Metall-Systemen regeln, kurz diskutiert. Auf der Basis der Kombination der Gibbs'schen und Langmuir'schen Adsorptionsisothermen mit Girifalco's und Good's Ausdruck für die Grenzflächenspannung zwischen nicht mischbaren Flüssigkeiten wird ein Modell vorgestellt, das mit Literaturdaten übereinstimmt, und mit dem sowohl die Grenzflächenspannung als auch der Kontaktwinkel zwischen flüssiger Schlacke und flüssigem Eisen im System $\text{CaO-CaF}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ berechnet werden können. Die Anwendung dieser Näherung auf Systeme, die FeO in der Schlacke und Kohlenstoff im Metall enthalten, wird anschließend diskutiert.

The rates of many high temperature reactions are influenced by interfacial phenomena. The presence of solutes such as oxygen, sulfur, selenium and tellurium, which segregate to a free surface in a liquid metal, have been shown to drastically reduce reaction rates in many important interfacial reactions and also to cause marked decreases in interfacial tension¹⁾²⁾. In addition, when surface active solutes enter into reactions, surface tension driven flows and instabilities can lead to large increases in reaction rate due to increased turbulence at the interface¹⁾³⁾⁴⁾. Therefore, in a wide variety of reactions, it is necessary to determine the effect of variations in interfacial properties on reaction rates. In the new steelmaking techniques under consideration a knowledge of the types of interfacial phenomena and the values of the metal-slag interfacial tension in the systems of interest will allow a better fundamental understanding of the process.

In this article the contact angle and the interfacial tension between liquid slags and liquid iron will be briefly reviewed and a model developed to aid in the prediction of slag-metal interfacial properties. At first the equilibrium condition will be discussed and a model developed for the calculation of interfacial tension in liquid iron – $\text{CaO-SiO}_2\text{-CaF}_2\text{-Al}_2\text{O}_3$ systems. The effect of dissolved carbon in the liquid iron and FeO in the slag on the iron-slag interfacial tension and the dynamic effects which can be expected in these systems will also be discussed.

Interfacial properties

Contact angle. Young's equation. It is commonly observed that when a liquid is placed on a solid, it forms a droplet which has a specific equilibrium shape and angle of contact, see figure 1. Droplets of water or mercury sitting on a flat glass surface are common examples. The equilibrium contact angle, θ , is a measure of the ability



solid

Figure 1. Schematic of a sessile drop

Bild 1. Schema eines aufliegenden Tropfens

of a liquid to wet a solid and varies from 0° , where the liquid wets the solid completely, to 180° , where there is only one point of contact between the liquid and the solid. Usually contact angles which are less than 90° are referred to as wetting and greater than 90° as non-wetting. Values of equilibrium contact angles for a number of important steelmaking and casting systems are given in tables 1–3.

The interfacial tensions can be considered as forces and a force balance at the contact point leads to Young's equation¹⁹⁾:

$$\gamma_{\text{metal-slag}} = \gamma_{\text{metal-gas}} - \gamma_{\text{slag-gas}} \cos \theta, \quad (1)$$

where $\gamma_{\text{metal-slag}}$ is the interfacial tension between the solid metal and the liquid slag droplet described in figure 1. $\gamma_{\text{metal-gas}}$ and $\gamma_{\text{slag-gas}}$ are the interfacial tensions between the metal and the slag with the gas phase respectively. This equation can also be derived by minimizing free energy and a number of detailed derivations are available^{16)–18)}. The contact angle is a fundamental parameter which relates the system's interfacial tensions. The sessile drop, as shown in figure 1, is commonly used to measure contact angles and to calculate values of interfacial tension²⁰⁾²³⁾²⁴⁾.

Neumann's relations. When a liquid is placed upon a liquid, a lens is formed if the liquids are immiscible. Common examples are oil on water and slag floating on liquid steel. Contact angle measurements are more difficult in liquid-liquid systems as the lens formed displaces the denser liquid, according to Archimedes principle, and the visible contact angle, α , is less than the actual contact angle, θ ,

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Table 1. Refractories in contact with liquid steel

Tafel 1. Feuerfestmaterial in Kontakt mit flüssigem Stahl

Refractory	temperature (°C)	contact angle	steel type
Al ₂ O ₃	1600	135	pure ⁸⁾ ⁷⁾ ¹⁰⁾ ¹¹⁾
SiO ₂	1600	115	pure ⁸⁾
CaO	1600	132	pure ⁸⁾
TiO ₂	1600	84	pure ⁹⁾
Cr ₂ O ₃	1600	88	pure ¹⁰⁾
ZrO ₂	1550	122	pure ¹¹⁾
MgO	1600	125	pure ¹¹⁾
MnO	1550	113	pure ¹²⁾
SiC 91%	1500	60	0.16% C ⁵⁾
graphite	1460	120	0.16% C ⁵⁾
TiN	1550	132	pure ¹²⁾
BN	1550	112	pure ²¹⁾
CaS	1550	87	pure ²²⁾
CaO-MgO-SiO ₂	1450	104-120	Ni-Cr steel ¹⁸⁾
CaO-SiO ₂ -Al ₂ O ₃	1450	96-114	Ni-Cr steel ¹⁹⁾

Table 2. Liquid slags in contact with liquid steel

Tafel 2. Flüssige Schlacken in Kontakt mit flüssigem Stahl

Slag type	temperature (°C)	contact angle	reference
CaO-Al ₂ O ₃ 36/64	1600	65	¹⁴⁾
CaO-Al ₂ O ₃ 50/50	1600	58	¹⁵⁾
CaO-Al ₂ O ₃ 58/42	1600	54	¹⁵⁾
CaO-Al ₂ O ₃ -SiO ₂	1600	43	¹⁴⁾
44/45/11			
CaO-Al ₂ O ₃ -SiO ₂	1600	40	¹⁴⁾
40/40/20			
CaO-Al ₂ O ₃ -SiO ₂	1600	36	¹⁵⁾
33/33/33			
CaO-Al ₂ O ₃ -SiO ₂	1600	13	¹⁴⁾
26/26/49			
CaO-SiO ₂ 58/42	1600	29	¹⁴⁾
CaO-SiO ₂ 50/50	1600	31	¹⁴⁾
CaO-CaF ₂ 5/95	1600	47	¹⁵⁾
CaO-CaF ₂ -Al ₂ O ₃	1600	36	¹⁵⁾
11/87/2			
CaO-CaF ₂ -Al ₂ O ₃	1600	28	¹⁵⁾
14/71/15			
CaO-CaF ₂ -Al ₂ O ₃	1600	34	¹⁵⁾
15/56/30			
CaO-CaF ₂ -Al ₂ O ₃	1600	41	¹⁵⁾
45/8/47			

Table 3. Liquid slags in contact with solid surfaces

Tafel 3. Flüssige Schlacken in Kontakt mit festen Oberflächen

Slag type	refractory type	temperature (°C)	contact angle
FeO-SiO ₂ 70/30	alumina	1250	<10 ¹⁶⁾
FeO-MnO-CaO-SiO ₂	zirconia	1500	5-20 ²⁾
-Al ₂ O ₃			
FeO-MnO-CaO-SiO ₂	alumina	1500	<10 ⁵⁾
-Al ₂ O ₃			
FeO-MnO-CaO-SiO ₂	SiC	1500	104-122 ²⁾
-Al ₂ O ₃			
FeO-MnO-CaO-SiO ₂	graphite	1500	110-132 ²⁾
-Al ₂ O ₃			
CaO-SiO ₂ -Al ₂ O ₃	MgO	1400	9-32 ²⁶⁾
40/40/20			
CaO-SiO ₂ -MgO	Si ₃ N ₄	1550	50 ²⁷⁾
10/56/34			
Na ₂ O-SiO ₂ -MgO	Si ₃ N ₄	1550	20 ⁵²⁾
mold slag	steel	1400	0-30 ¹⁷⁾
CaO-SiO ₂ -Al ₂ O ₃	iron	1450	30-60 ⁵³⁾
40/40/20			
CaO-SiO ₂ -Al ₂ O ₃ -FeO	iron	1450	0-60 ⁵³⁾

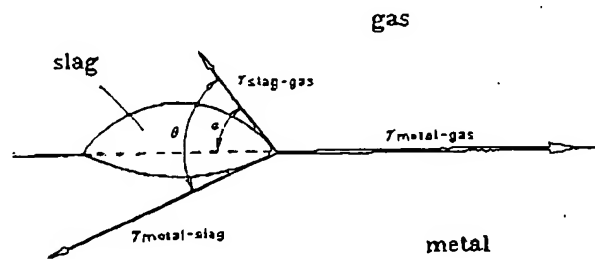


Figure 2. Schematic of a liquid lens

Bild 2. Schema einer flüssigen Linse

as can be seen in figure 2. However, it is possible to measure both the interfacial tension and the contact angle from lens measurements¹⁵⁾. Since the interfacial tensions can be described as force vectors, the following relations result from geometrical considerations where, if horizontal equilibrium is considered, Neumann's relation results:

$$[\gamma_{\text{metal-slag}}]^2 = [\gamma_{\text{metal-gas}}]^2 + [\gamma_{\text{slag-gas}}]^2 - 2 \gamma_{\text{metal-gas}} \gamma_{\text{slag-gas}} \cos \alpha, (2)$$

and, if the metal surface remains horizontal near the edge of the drop, the following relationship relates θ to α , if vertical equilibrium is considered:

$$\gamma_{\text{metal-slag}} \sin (\theta - \alpha) = \gamma_{\text{slag-gas}} \sin \alpha. (3)$$

The contact angles reported in tables 1 to 3 are either from sessile drop or lens measurements at low steel oxygen and sulphur contents. Contact angles are greater than 90° for most solid refractory oxides in contact with liquid iron and less than 90° for liquid slags in contact with liquid iron. Liquid slags wet liquid and solid steel (tables 2 and 3). Contact angle is decreased with increasing silica content in the slag and increasing oxygen content in the metal, and increased with increasing sulphur content in the metal and alumina content in the slag. The effect of dissolved sulphur and oxygen content on the contact angle between liquid iron and a CaO-Al₂O₃-SiO₂-FeO slag is shown in figures 3 and 4.

Interfacial tension. Once the contact angle is determined, only two other interfacial tensions are necessary to determine the other interfacial tension in liquid-solid and liquid-liquid systems. Interfaces which are not wet have high interfacial tensions, greater than either of the component interfacial tensions, while interfaces which are wet, have lower interfacial tensions than the higher of the component interfacial tensions. The interfacial tensions of a number of pure systems are given in table 4. It is easier to measure liquid-gas than liquid-liquid interfacial energies. Therefore the goal of this work was to calculate liquid-liquid interfacial energies from a knowledge of liquid-gas interfacial tensions.

Liquid iron. The surface tension of pure liquid iron is dependent on purity as small additions of oxygen, sulphur, selenium and tellurium significantly reduce its value. The exact value for the interfacial tension of pure iron depends upon the experimental technique as oscillating droplets give higher surface tension values than sessile droplets. In this paper, as all available data on interfacial tension in liquid-liquid systems was from sessile droplets, correlations are based only on sessile drop measurements.

Table 4. Interfacial tensions of some pure systems

Tabelle 4. Grenzflächenspannungen einiger reiner Systeme

System	temperature (°C)	γ (mN/m)
Al ₂ O ₃ (s)	1475	930 ²⁷⁾
Al ₂ O ₃ -Fe(l)	1570	2300 ²⁵⁾
MgO-Fe(l)	1725	1600 ²⁵⁾
MgO(s)	25	1000 ²⁶⁾
Fe(l)	1600	1890 ²⁸⁾
b-Fe(s)	1400	2150 ²⁵⁾
CaO-SiO ₂	1600	485 ³⁰⁾
FeO	1600	570 ²⁵⁾
CaO-SiO ₂ -Al ₂ O ₃	1550	500 ³²⁾
CaO-Al ₂ O ₃	1550	600 ³³⁾
CaF ₂	1550	280 ³³⁾
CaO-CaF ₂ 20/80	1550	310 ³³⁾
CaO-Al ₂ O ₃ -CaF ₂	1550	400 ³³⁾
40/40/20		
CaO-Al ₂ O ₃ -CaF ₂	1550	300 ³³⁾
20/20/60		

Belton has shown that for liquid metals the effect of group VI solute elements on interfacial tension can be described by combination of the Gibbs and Langmuir adsorption equations²⁴⁾:

$$\gamma_p - \gamma = RT \Gamma_i^0 \ln [1 + K_i a_i], \quad (4)$$

where γ and γ_p are the surface tensions of the solution and pure solvent, respectively, Γ_i^0 is the saturation coverage, K_i is the adsorption coefficient of the solute and a_i is the activity of the solute. For example, the results of Kasama et al. who measured the surface tension of liquid iron as a function of oxygen content at 1600 °C²⁸⁾ using an oscillating droplet technique, can be satisfactorily explained by the following equation:

$$1890 - \gamma = 299 \ln (1 + 110 [\%O]) \text{ mN/m}, \quad (5)$$

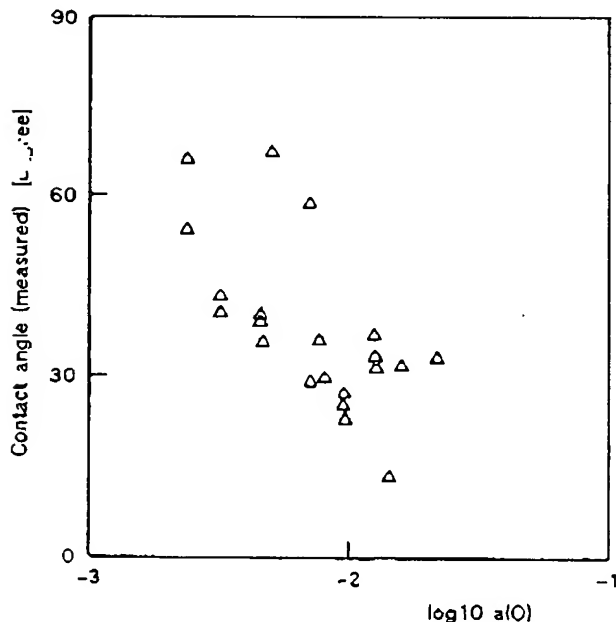


Figure 3. Effect of oxygen on the contact angle between liquid slag and liquid iron. Based on data of Gaye et al.¹¹⁾

Bild 3. Einfluß von Sauerstoff auf den Kontaktwinkel zwischen flüssiger Schlacke und flüssigem Eisen. Nach Gaye et al.¹¹⁾

where the value of the absorption coefficient is in good agreement with that found by Cramb et al., namely 98, during kinetic studies³⁵⁾ and Kawai, namely 102, from interfacial studies³⁶⁾. Sessile drop results, although yielding a lower γ_p value, are also in agreement with this form of equation and yield absorption coefficients similar to those found from oscillating droplets. Equations of this type were first used by Szyskowski (1908) in aqueous solution³⁷⁾ and by Kurkjian and Kingery (1956) to describe similar effects in liquid nickel alloys³⁸⁾. The following equations can be used to describe the variation of the adsorption coefficient with temperature:

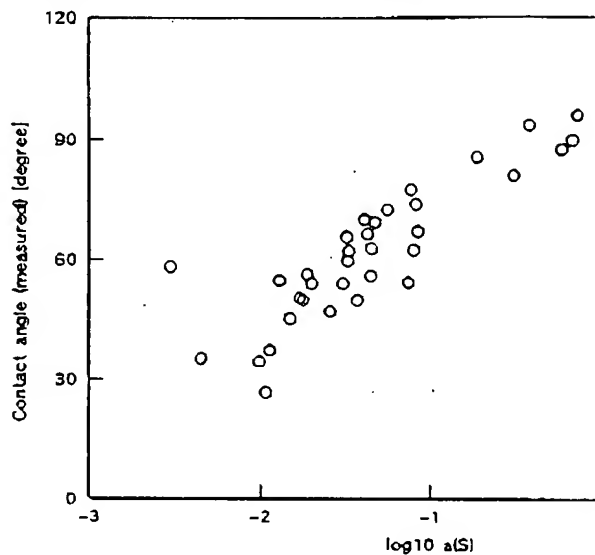


Figure 4. Effect of sulphur on the contact angle between liquid iron and liquid slag. Based on data of Gaye et al.¹¹⁾

Bild 4. Einfluß von Schwefel auf den Kontaktwinkel zwischen flüssigem Eisen und flüssiger Schlacke. Nach Gaye et al.¹¹⁾

adsorption coefficient for oxygen on liquid iron

$$\log K_0 = \frac{11370}{T} - 4.09, \quad (6)$$

where the absorption coefficient is with respect to the 1wt.% ideal solution standard state³⁵⁾.

adsorption coefficient for sulphur on liquid iron

$$\log K_s = \frac{5874}{T} - 0.95, \quad (7)$$

where the absorption coefficient is with respect to the 1 wt.% standard state and the equation is based on regression of available literature values.

The following equations, from studies of sessile droplet data, were used in this work to represent the surface tensions in oxygen and sulphur containing systems at 1550 °C^{39,40)}:

$$1788 - \gamma = 281 \ln (1 + K_0 [\%O]) \text{ mN/m} \quad (8)$$

for the effect of oxygen on the surface tension of liquid iron, and,

$$1788 - \gamma = 195 \ln (1 + K_s [\%S]) \text{ mN/m} \quad (9)$$

for the effect of sulphur on the surface tension of liquid iron.

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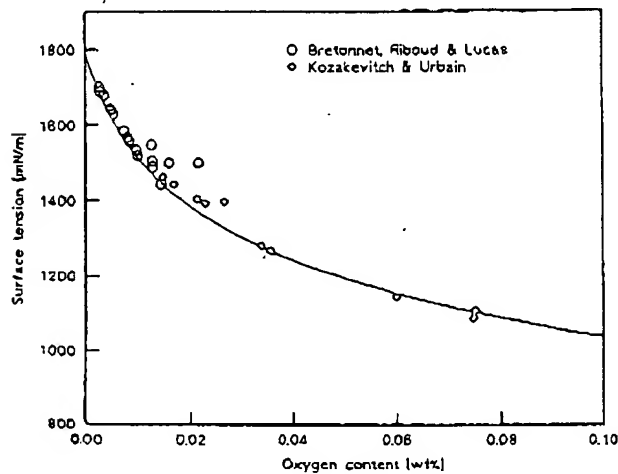


Figure 5. Effect of oxygen on the surface tension of pure iron at 1550 °C

Bild 5. Einfluß von Sauerstoff auf die Oberflächenspannung von Reineisen bei 1550 °C

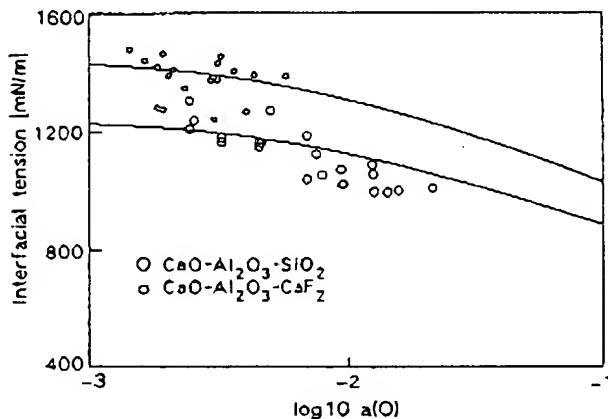


Figure 6. Effect of oxygen on interfacial tension between liquid iron and liquid slag at 1800 °C

Bild 6. Einfluß von Sauerstoff auf die Grenzflächenspannung zwischen flüssigem Eisen und flüssiger Schlacke bei 1800 °C

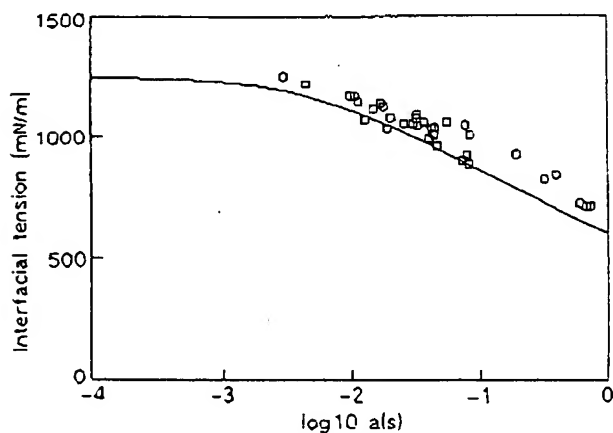


Figure 7. Effect of sulphur on interfacial tension between liquid iron and liquid slag at 1600 °C

Bild 7. Einfluß von Schwefel auf die Grenzflächenspannung zwischen flüssigem Eisen und flüssiger Schlacke bei 1600 °C

An example of the close correlation between equation (8) and measured data is given in figure 5. To calculate interfacial tensions in the system Fe-O-S, it is assumed that the reductions in surface tension are additive in the ternary system, following the results of Keene et al.⁴¹⁾

Liquid slags. The interfacial tensions of a number of slag systems have been recently reviewed by K. C. Mills and B. J. Keene⁴¹⁾⁻⁴³⁾. Slags of interest are in the CaO-CaF₂-SiO₂-MgO-Al₂O₃ family but can also contain quantities of MnO and FeO. Generally silica, calcium fluoride, sodium oxide and phosphorus pentoxide reduce slag surface tensions. This behaviour is very complex and not yet easily calculated, therefore, slag interfacial tensions used in this study are the measured values. Correlations of the interfacial tension of slags have been attempted by Eales⁴⁴⁾ and Sato⁴⁵⁾. Care must be taken in extrapolating these correlations outside of the data base from which they were developed. A number of representative slag interfacial tensions are given in table 4. Values range from 280 mN/m for calcium fluoride to 600 mN/m for calcium aluminate at 1550 °C.

Metal-slag interfaces. The interfacial tensions of liquid slag-liquid metal systems have been measured by a number of French, Russian and Japanese investigators³³⁾⁻³⁵⁾, ³³⁾³⁶⁾⁴⁰⁾⁴²⁾. Interfacial tension is a function of slag and metal composition, decreasing with increasing silica content in the slag and increasing oxygen and sulphur contents in the metal. In figure 6 the variation of interfacial tension with oxygen content is plotted as a function of log a_O for CaO-Al₂O₃-CaF₂ and CaO-Al₂O₃-SiO₂ slags. The slag-metal interfacial tension is higher for CaF₂ containing slags. In figure 7 slag-metal interfacial tension is plotted as a function of log a_S for CaO-Al₂O₃-SiO₂ slags. In these figures the large effect of oxygen and sulphur on interfacial tension can be seen.

There have been a number of attempts to determine a relationship which could be used to calculate the interfacial tension of two immiscible liquids from a knowledge of the individual interfacial tensions.

Rayleigh's relation: The first attempted relationship was by Lord Rayleigh⁴⁶⁾:

$$\gamma_{\text{slag-metal}} = \gamma_{\text{slag-gas}} + \gamma_{\text{metal-gas}} - 2 [\gamma_{\text{metal-gas}} \cdot \gamma_{\text{slag-gas}}]^{0.5} \quad (10)$$

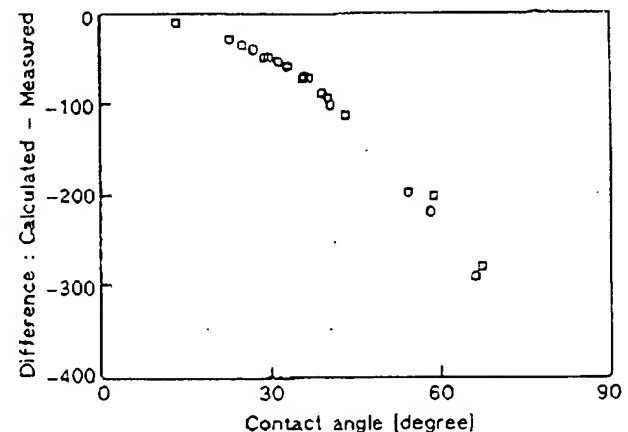


Figure 8. Antonow's law

Bild 8. Antonow's Gesetz

This relation was empirical and found later by Lord Rayleigh to be a poor fit to the data available at that time.

Antonow's relation: The interfacial tension between two immiscible liquids was also estimated by Antonow⁴⁷):

$$\gamma_{\text{metal-slag}} = \gamma_{\text{metal-gas}} - \gamma_{\text{slag-gas}} \quad (11)$$

This is a simplification of Young's and Neumann's equation for the case where θ and thus α tends to zero, i.e. complete wetting. In figure 8, $[\gamma_{\text{metal-gas}} - \gamma_{\text{slag-gas}} - \gamma_{\text{metal-slag}}]$ or $\Delta\gamma$ is plotted as a function of contact angle for a number of slag systems. A value of zero indicates adherence to Antonow's rule. At low values of θ ($<20^\circ$) Antonow's rule is a fair estimation of interfacial tension and is useful for high FeO containing slags⁴⁰). However, for all other slag chemistries, this representation of interfacial tension is not useful.

Girifalco and Good's relation: Girifalco and Good have developed a more general expression for estimation of interfacial tension where they considered the interfacial tension between immiscible liquids to be due to London dispersion forces and postulated that the free energy of adhesion between the two phases (ΔG_{12}^a) might be given by the geometric mean of the free energy of cohesion of the separate phases (ΔG_1^c or ΔG_2^c) in a manner similar to Berthelot's relation for attractive constants in the van der Waals equation^{48,49}). Thus, for slag metal systems.

$$|\Delta G_{\text{slag-metal}}^a| = \sqrt{\Delta G_{\text{slag-gas}}^c \cdot \Delta G_{\text{metal-gas}}^c} \quad (12)$$

For slag-metal systems

$$\begin{aligned} -\Delta G_{\text{metal-gas}}^c &= 2\gamma_{\text{metal-gas}} \\ -\Delta G_{\text{slag-gas}}^c &= 2\gamma_{\text{slag-gas}} \\ -\Delta G_{\text{metal-slag}}^a &= \gamma_{\text{metal-gas}} + \gamma_{\text{slag-gas}} - \gamma_{\text{metal-slag}} \end{aligned}$$

By combining these relations with equation (12), Lord Rayleigh's relation (equation(10)) results.

Girifalco and Good's contribution was in the realization that the ratio of the free energy of adhesion between the two phases and the geometric mean of free energies of cohesion of the separate phases is a unique property (Φ) of the system, where:

$$\Phi = \frac{-\Delta G_{\text{slag-metal}}^a}{\sqrt{\Delta G_{\text{metal-gas}}^c \cdot \Delta G_{\text{slag-gas}}^c}} \quad (13)$$

Thus, in Girifalco and Good's approach the following equation describes the relationship between interfacial tensions:

$$\gamma_{\text{metal-slag}} = \gamma_{\text{metal-gas}} + \gamma_{\text{slag-gas}} - 2\Phi(\gamma_{\text{metal-gas}} \cdot \gamma_{\text{slag-gas}})^{0.5}, \quad (14)$$

where Φ is characteristic of the system. Φ tends to zero when there is no interaction between the phases and increases as the attraction between the phases increases.

Application of Girifalco and Good's model. $\text{CaO}-\text{CaF}_2-\text{SiO}_2-\text{Al}_2\text{O}_3$ - liquid iron. Girifalco and Good's treatment of interfacial tension was applied to liquid iron-slag systems. Φ was calculated from Girifalco and Good's relation by assuming that the total interfacial tension could be split into three parts: the pure metal, the effect of oxygen or sulphur on the pure metal and then the interaction between metal droplet and slag. From the measured data of Gaye et al., Φ was calculated and found to vary between 0.4 and 0.6 for $\text{CaO}-\text{CaF}_2-\text{SiO}_2-\text{Al}_2\text{O}_3$ sys-

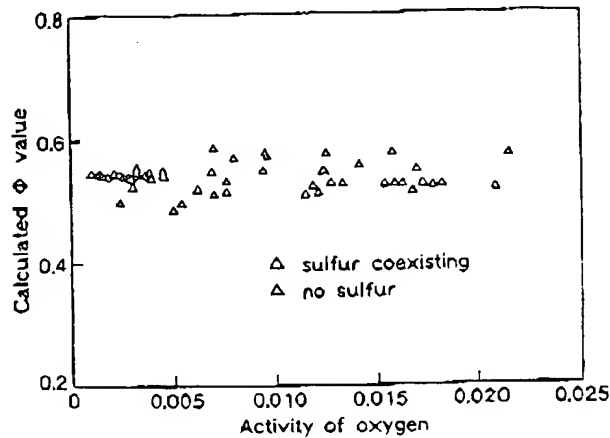


Figure 9. Φ as a function of dissolved oxygen content

Bild 9. Φ als Funktion des Gehalts an gelöstem Sauerstoff

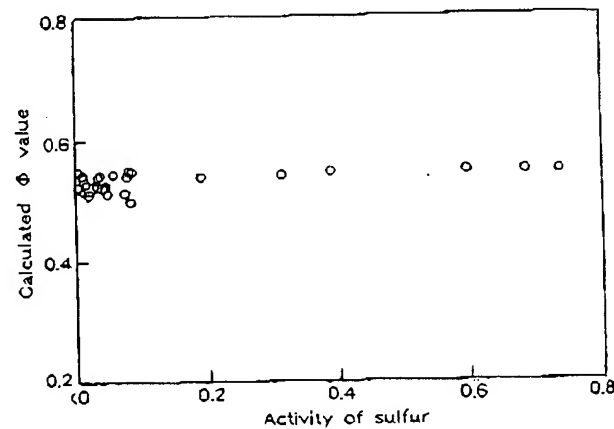


Figure 10. Φ as a function of dissolved sulphur content

Bild 10. Φ als Funktion des Gehalts an gelöstem Schwefel

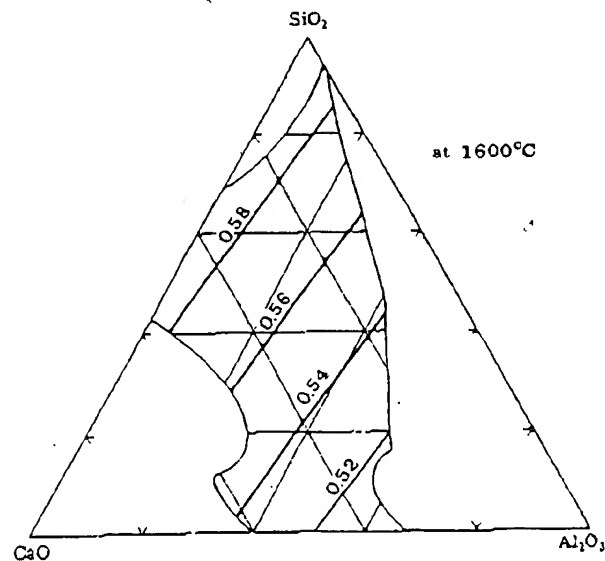


Figure 11. Iso- Φ lines in the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ ternary at 1600°C

Bild 11. Iso- Φ -Linien im Dreistoffsystem $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ bei 1600°C

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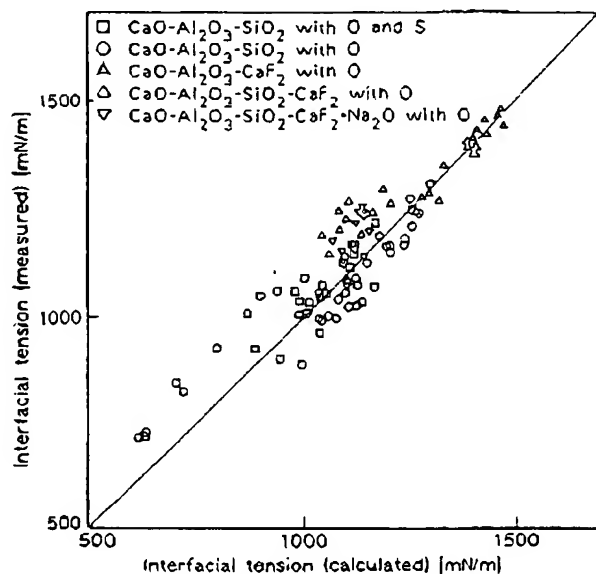


Figure 12. Calculated vs. measured interfacial tension values for slag-iron system at 1600 °C. From the data of Gaye et al.¹¹⁾

Bild 12. Vergleich der berechneten und der gemessenen Grenzflächenspannung für ein Schlacke-Eisen-System bei 1600 °C. Nach Daten von Gaye et al.¹¹⁾

tems. As can be seen in figures 9 and 10, ϕ values were apparently independent of metal oxygen and sulphur contents over the range of their data. In the case of oxygen variation this cannot be strictly correct as there must be an equilibrium FeO content in the slag. However, at these low levels, this effect is negligible and will be ignored at this time. An example of the variation of ϕ with slag composition is given in figure 11 where iso- ϕ lines are drawn on a CaO-Al₂O₃-SiO₂ ternary. ϕ increases with increasing silica content and decreases with increasing alumina content in accord with the variation in contact angle in these systems where additions of silica reduce the contact angle and additions of alumina increase the contact angle. The following equations were developed for calculation of ϕ by regression analysis of Gaye's data: for the SiO₂-CaO-Al₂O₃ ternary

$$\phi = 0.004676 (\% \text{Al}_2\text{O}_3) + 0.005973 (\% \text{SiO}_2) + 0.005806 (\% \text{CaO}); \quad (15)$$

for the CaO-CaF₂-Al₂O₃ ternary

$$\phi = 0.003731 (\% \text{Al}_2\text{O}_3) + 0.003900 (\% \text{CaF}_2) + 0.006904 (\% \text{CaO}). \quad (16)$$

The CaO-CaF₂-SiO₂-Al₂O₃ quaternary can be developed by interpolation and interfacial tensions in systems of interest can be calculated using Belton's equation, a knowledge of ϕ and the slag surface tension. An example of the ability to calculate slag-metal interfacial tensions by this method is given in figures 6 and 7, where the solid lines are the calculated values assuming an average slag composition and the points are from the data of Gaye et al.¹⁵⁾ Data scatter can be explained due to the compositional variations in the experimental data. In figure 12, calculated interfacial tension values for specific compositions are plotted versus actual values for a number of slag

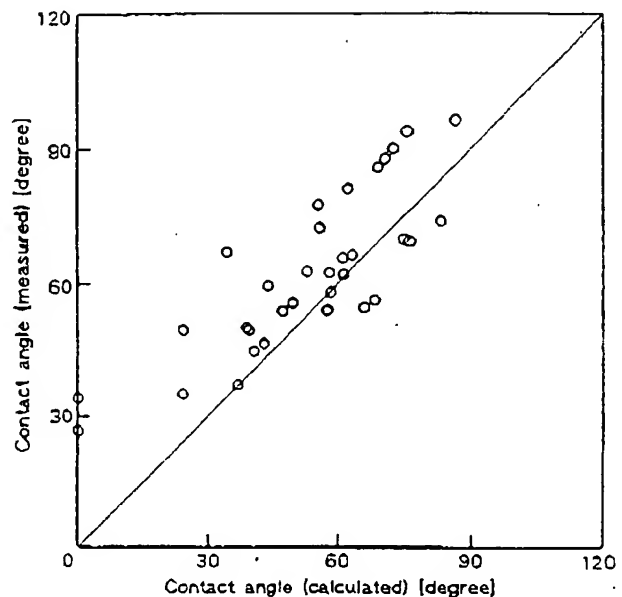


Figure 13. Calculated vs. measured contact angle

Bild 13. Vergleich zwischen berechnetem und gemessenem Kontaktwinkel

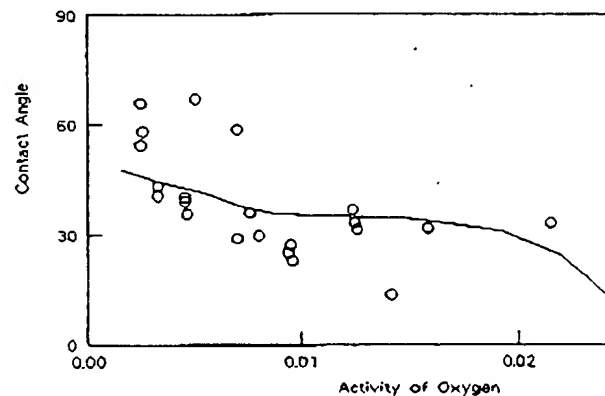


Figure 14. Contact angle as a function of oxygen activity in CaO-SiO₂-Al₂O₃ systems

Bild 14. Kontaktwinkel als Funktion der Sauerstoffaktivität in CaO-SiO₂-Al₂O₃-Systemen

metal systems. The calculated values are in good agreement with the actual values and, the combination of Girifalco and Good's approach with Belton's approach leads to an adequate first order approximation of interfacial energies for pure iron with CaO-CaF₂-SiO₂-Al₂O₃ slags. Utigard and Toguri have also adapted Girifalco and Goods model to slag-metal systems, however, their approach is not as easy to adapt to complex systems⁵¹⁾⁵²⁾.

Girifalco and Good's approach (equation (14)) allows metal-slag interfacial tension to be calculated from a knowledge of slag-metal and slag-gas interfacial tension. Once $\gamma_{\text{metal-slag}}$ is calculated, by using equations (2) and (3), θ can also be calculated. An example of the relationship between the predicted θ and the value calculated from visible contact angle (α) measurements is given in figure 13. Calculated θ values from interfacial measure-

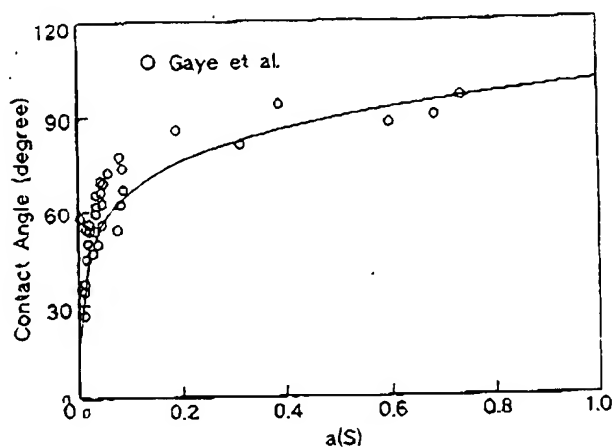


Figure 15. Contact angle as a function of sulphur activity in CaO-SiO₂-Al₂O₃ systems

Bild 15. Kontaktwinkel als Funktion der Schwefelaktivität in CaO-SiO₂-Al₂O₃-Systemen

ments are in good agreement with Gaye's calculated values¹⁵⁾, again showing internal consistency between Gaye's data and the approach of Girifalco and Good. Care must be taken in carrying out these calculations to ensure that the equilibrium condition is calculated, e.g. in the slag system CaO-SiO₂-Al₂O₃ it is not possible to hold the slag composition constant while varying the oxygen content in the metal. In figure 14 the contact angle for liquid iron in contact with CaO-SiO₂-Al₂O₃ slags is plotted as a function of the activity of oxygen in the metal. The line drawn on the graph is calculated for a CaO to Al₂O₃ ratio of 1 assuming equilibrium in the CaO-SiO₂-Al₂O₃ system while the data points are for a variety of slag compositions in this system. It is easier to calculate the effect of sulphur on contact angle at low oxygen contents as the equilibrium condition is easier to specify assuming that the effect of sulphur on slag surface tension is minor. In figure 15 the contact angle is plotted as a function of the activity of sulphur in the CaO-SiO₂-Al₂O₃ system for a 1:1:1 composition and assuming 30 ppm oxygen. The data scatter can be explained by the chemical variation in the data away from the 1:1:1 composition. The agreement between calculated and measured results is very good.

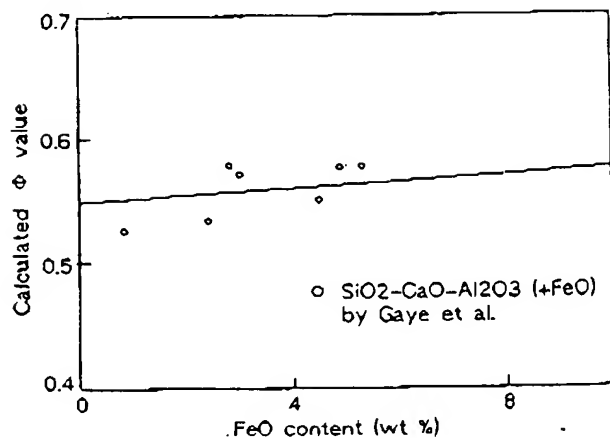


Figure 16. Effect of FeO content on Φ value

Bild 16. Einfluß des FeO-Gehaltes auf den Φ -Wert

Thus by assuming a simple model of interfacial tension, Φ can be shown to be a simple function of slag chemistry which can then be used to determine interfacial tension and contact angles in liquid iron-slag systems via Girifalco and Good's model.

Effect of Fe₂O additions to slag. The data discussed so far contained small quantities of dissolved oxygen (<0.03%) and small quantities of Fe₂O in equilibrium in the slag. However, as has been shown by Ogino⁴⁰⁾ and discussed by Mills⁴²⁾ the addition of FeO to a slag results in marked decreases in the interfacial tension between liquid iron and the slag. Ogino noted $\gamma_{\text{metal-slag}}$ to drop from 1400 mN/m to 500 mN/m upon addition of 7% FeO to a CaO-Al₂O₃ slag. After 15 minutes, as the system approached equilibrium, the value of $\gamma_{\text{metal-slag}}$ increased to 870 mN/m. The oxygen content of the metal is determined by the FeO concentration in the slag and at low oxygen contents the effect on Φ on the FeO content of the slag can be ignored. However, at higher FeO contents this effect must be taken into account.

At high FeO contents the contact angle between the slag and liquid iron tends to zero. In this case Neumann's relation (equation (2)) reduces to Antonow's relation (equation (11)). If one combines equation (2) with equation (14), it follows that, at high FeO contents, using the data of Ogino et al.⁴⁰⁾:

$$\Phi = \sqrt{\frac{\gamma_{\text{slag-gas}}}{\gamma_{\text{metal-gas}}}} = \sqrt{\frac{610}{910}} = 0.82. \quad (17)$$

Since $\gamma_{\text{metal-gas}} \approx \gamma_{\text{slag-gas}}$ it follows that $\Phi \approx 1$ and in these systems the maximum value of Φ is 0.82. Thus at high FeO contents Φ tends to 0.82.

Since the maximum value of Φ at 100% FeO is easily determined, a first approximation to the effect of FeO on a CaO-SiO₂-Al₂O₃ slag can be attempted by assuming that Φ increases linearly with FeO content along a plane of constant component ratio such as CaO-SiO₂-Al₂O₃ = 1. The data of Gaye et al. is plotted in this manner in figure 16 and shows a fair agreement between calculated and measured Φ values. In order to test the applicability of this method to higher oxygen contents the results of Ogino were applied to this model. The value of Φ was calculated assuming a linear extrapolation between the

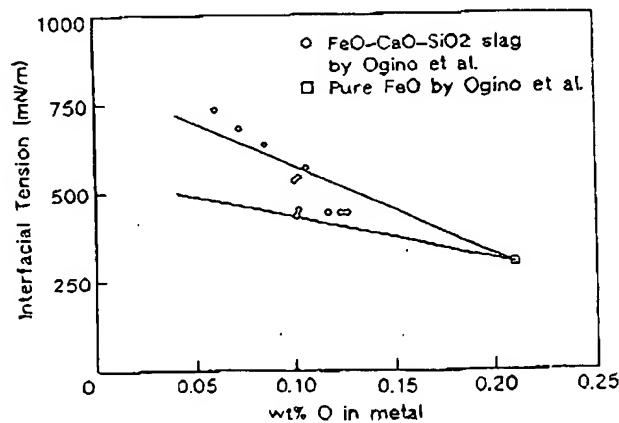


Figure 17. Interfacial tension at high oxygen contents

Bild 17. Grenzflächenspannung für hohe Sauerstoffgehalte

Process metallurgy

base Φ value and the value for pure FeO in the following manner:

$$\Phi_{\text{sys}} = \Phi_{\text{base}} + \frac{(0.82 - \Phi_{\text{base}}) \cdot \% \text{FeO}}{100} \quad (18)$$

Φ_{sys} is the Φ value for the system once FeO has been added and Φ_{base} is the Φ value for the system calculated by regression. The results of this method are given in figure 17 where the interfacial tension was calculated for a range of compositions close to Ogino's data⁴⁰). Exact calculation was not possible as complete slag chemical analysis was not given. However the lines are calculated assuming the data fall within the liquid portion of the phase diagram. The surface tensions of the metal as determined by Ogino were used as Belton's equation is not accurate at such high oxygen contents. Good agreement between Ogino's data and this approach to the calculation of slag-metal interfacial tension at high oxygens or high FeO contents can be seen in figure 18 where Ogino's data is close to the calculated range.

Effect of carbon content. The effect of carbon on interfacial tension has been documented by Bretonnet et al. for CaO-Al₂O₃-SiO₂ slags¹³). Interfacial tension was found to decrease with increasing SiO₂ content in the slag and increase with carbon content in the steel. The effect of slag SiO₂ content decreased as carbon content increased and at carbon saturation the interfacial tension was independent of silica content (figure 18). Contact angle increased slightly with increasing carbon content reaching a maximum value of 70° at carbon saturation, see figure 19.

The effect of carbon is difficult to understand. Carbon itself has only a very moderate effect on the surface tension of liquid iron^{53,54}). This moderate effect has been interpreted as evidence of the lack of surface segregation of carbon in liquid iron; however, the effect of carbon on slag-metal interfacial tension is quite remarkable if carbon does not segregate. For example, the decrease in interfacial tension and contact angle between the slag and the metal with increasing slag silica content at low metal carbon contents is evident for increased bonding, perhaps by dipole interaction, between the slag and the metal. The effect of carbon addition is to increase interfacial tension and contact angle, indicating less bonding between the metal and the slag. The elimination of the effect of silica indicates a fundamental change in the nature of the surface of the liquid metal as carbon is added. This change in the nature of the surface of the liquid metal does not affect the primary bonding mechanism of the surface of the liquid metal as the decrease in surface tension of the metal with carbon addition is very small. The change is indicative of a second order effect which does not affect metal surface tension but controls the ability of the surface of the liquid iron to associate with the liquid slag and thus has a strong effect on interfacial tension between slag and metal. At this time, due to a paucity of data and inspiration, no method has been developed to incorporate the effect of carbon into a model of interfacial tension.

Dynamic effects

During high rates of mass transfer the interfacial tension between slag and metal can decrease below the equilibrium levels. This phenomenon has been well documented by

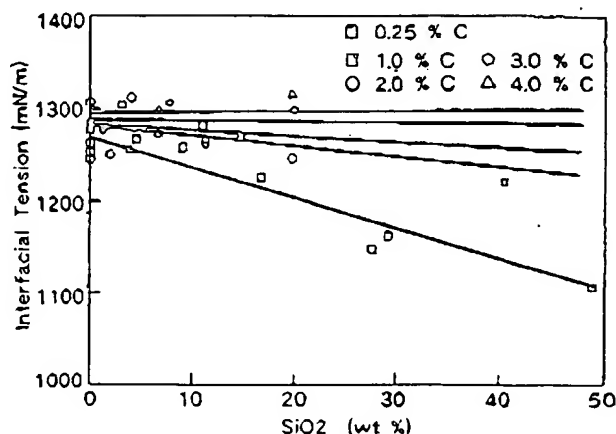


Figure 18. Effect of carbon content on interfacial tension

Bild 18. Einfluß des Kohlenstoffgehaltes auf die Grenzflächenspannung

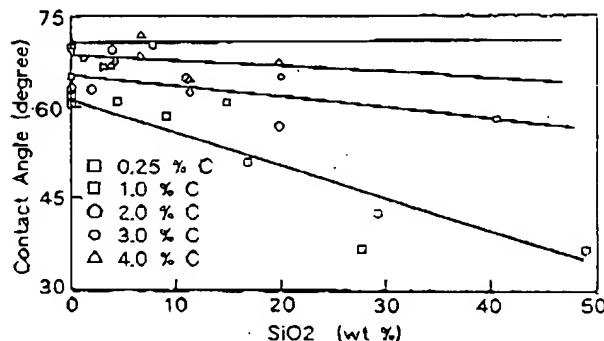


Figure 19. Effect of carbon content on contact angle

Bild 19. Einfluß des Kohlenstoffgehaltes auf den Kontaktwinkel

Riboud and Lucas³) and Brimacombe⁴). Fluctuations in interfacial tension can enhance mass transfer via the Marangoni effect or by spontaneous emulsification at very high rates of mass transfer. These effects may be very important in understanding reaction rates in the new steel-making processes, however, little is known about dynamic phenomena other than they may be expected at significant slag FeO levels in the new steelmaking processes. Reduced levels of interfacial tension will however increase the likelihood of liquid slag particle entrapment in the liquid steel and exacerbate the problems of separation of slag from metal after treatment while improving the foaming ability of the slag.

Conclusions

The approach of Girifalco and Good may be a useful aid in the calculation of interfacial tension and contact angles in slag-metal systems as it yields results which are consistent with current literature values if Φ is a simple function of slag chemistry. The proof of this approach will be when Φ can be calculated independently, however, until that time, correlations which allow the calculation of Φ for the liquid iron - CaO-SiO₂-Al₂O₃-FeO system, have been developed.

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